



A study of copper-exchanged mordenite natural and ZSM-5 zeolites as SCR-NO_x catalysts for diesel road vehicles: Simulation by neural networks approach

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ABSTRACT

Copper-catalysts, based on the ZSM-5 (CuZSM5) and Cuban natural Mordenite (CuMORD) zeolites have been prepared by a conventional ion-exchange method and their catalytic activity in the selective catalytic reduction (SCR) of NO was studied using ammonia in presence of H₂O and SO₂. A commercial catalyst SCR (CATCO) based on V₂O₅–WO₃–TiO₂, was also studied as reference. This paper presents experimental results using catalysts without the toxic vanadium and exploits a neural network based approach to predict NO_x conversion efficiency of three SCR catalysts. The derived mathematical functions are integrated in a numerical model for diesel road vehicle simulation to simulate diesel vehicles equipped with such SCR catalysts. The main results indicate that despite of toxic vanadium and N₂O formation, CATCO shows the better NO_x conversion efficiencies. However, CuMORD does not form N₂O and have better performance than the CuZSM5. The simulation results show lower level of NO_x for heavy-duty and light-duty diesel vehicles compared with homologation load cycles.

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1. Introduction

The main environmental problems for diesel engines are emissions of Nitrogen Oxides (NO_x) and particulates (PM). According to European Union statistics from 2003, transport (mainly road transport) contributes to 54% of total NO_x emissions, and industry to 23% [1]. NO_x emissions from the exhaust gas of a diesel engine are usually composed of more than 90% of NO [2]. NO is involved in the formation of ground-level ozone, acid rain, and contributes to the greenhouse effect [3]. Due to its adverse effects in the human health and in the environment, more restricted legislations concerning the emissions of NO from stationary and mobile sources have come out. However, advances in technology related to engines cannot further reduce NO_x emissions so it is necessary to utilize after-treatment systems.

The SCR of NO_x is the chosen technology by the majority of diesel bus and truck manufacturers in Europe to meet the legislation (see Table 1, Figs. 1 and 2). This is due to the high NO_x reduction achievable compared to the other NO_x reduction technology (exhaust gas regulations, EGR). It has been proven by track record that stationary applications and the SCR systems do

not provoke an increase in fuel consumption or sensitivity to sulphur as lean NO_x trap technology does [3,4]. In particular, SCR of NO using urea as reductant offers significant fuel savings (around 8% with respect to EGR systems), stable performance over extended mileage and compatibility with any engine setting [2,3]. As a matter of fact, availability of low sulphur fuel is gradually increasing within the EU, with the implementation of Euro IV making it possible to fill up with low-sulphur diesel at most filling stations in the EU countries (limited to a maximum of 10 ppm in 2009). This will be very important to assure the proper working of the SCR system [5,6].

For light-duty diesel vehicles (LDD) a chassis dynamometer test is used for emission testing and certification in Europe. It is composed of four ECE (Economic Commission for Europe) driving cycle, Urban Driving Cycles (UDC), simulating city driving, and one Extra Urban Driving Cycle (EUDC), simulating highway driving conditions. The cold-start version of the test, introduced in 2000, is also called New European Driving Cycle (NEDC), as it is shown in Fig. 1 [5].

The ESC (European Steady Cycle) test cycle was introduced in Directive 1999/96/EC amending Directive 8/77/EEC, together with the ETC (European Transient Cycle) and the ELR (European Load Response) tests, for emission certification of heavy-duty diesel engines (HDD). ESC test cycle comprises 13 steady-state loads, and the final result is a weighted average, as shown in Fig. 2a. The ETC

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Table 1
Legislation for diesel vehicles NO_x emissions in Europe.

Heavy-duty vehicle [g/kWh]	Cycles	Light-duty vehicle [g/km]	Cycles
2000 (Euro III)	5.0 ESC & ETC	2000 (Euro III) 0.50	NEDC
2005 (Euro IV)	3.5 ESC & ETC	2005 (Euro IV) 0.25	NEDC
2008 (Euro V)	2.0 ESC & ETC	2009 (Euro V) 0.18	NEDC
2013 (Euro VI) ^a	0.4 ESC& ETC	2014 (Euro VI) ^a 0.08	NEDC

^a Under discussion [5].

cycle has been developed by the FIGE Institute, Aachen, Germany, based on real road cycle measurements of heavy-duty vehicles [6]. Different driving conditions are represented by three parts of the ETC cycle, including urban, rural and motorway driving (see Fig. 2b) [5,7].

In Europe, the ETC test has been required, since the date mentioned above, for all new gas engine types, and for all new diesel engine types utilizing advanced emission control technology, meaning NO_x and/or particulate aftertreatment [5,7].

The amount of NO_x in the exhaust of the engines before the SCR catalyst can be measured in a dynamometer/test bench using NO_x gas analysers or can be estimated by simulation codes. The urea solution is dosed into the exhaust gases of the vehicle suffering decomposition and hydrolysis to form ammonia. If the ammonia/urea introduced into the system does not match the NO_x to be converted, then there will be some ammonia slip. In practice slightly less than 100% NO_x conversion is usually targeted [3,4].

Anatase supported vanadia-tungsta (i.e. V₂O₅ and WO₃) catalysts are the most frequently used for removal of NO_x from the out-gases of power plants, heat plants, nitric acid factories, stationary diesel engines and now also for lean exhaust gases of mobile diesel engines [4]. These typical catalysts show high efficiency conversion for NO at low temperatures. However, at high temperatures (>400 °C) this catalyst tends to form nitrous oxides (N₂O), a greenhouse gas [1,8]. A reduction in NO_x conversion efficiency can also be observed by a direct oxidation of ammonia [9].

Due to its toxicity, vanadium-based SCR catalysts will be removed from the HDD market in few years, due to its toxicity. On European passenger cars, however, it is expected that stringiest emission limits will be attained using non-toxic Zeolite-based technologies. Any application in USA and Japan (i.e. passenger cars and heavy-duty trucks) will use zeolite-based technologies, since

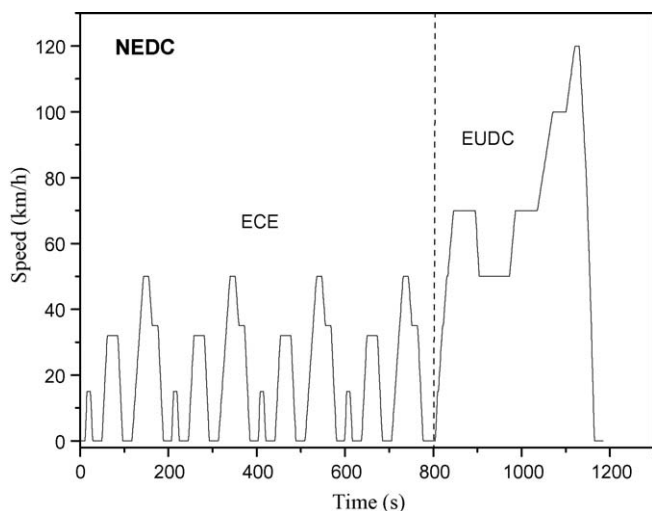


Fig. 1. NEDC driving cycle for light-duty diesel vehicles.

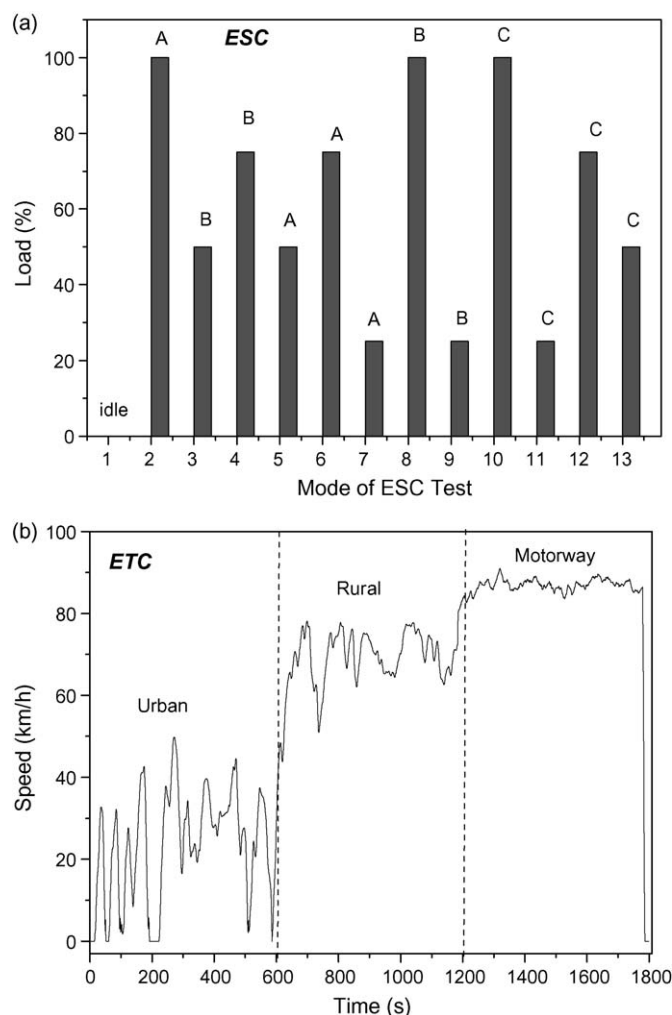


Fig. 2. (a) ESC (load and engine speed modes of 13-mode) test cycle used in heavy-duty engine and (b) simulates ETC cycle for engines vehicle speed versus time of FIGE cycle on chassis dynamometer [5].

vanadium is listed in the California Proposition 65 List as potentially carcinogenic substance [10]. On the so-called “emerging markets” such as China, India, and Brazil, vanadium-based catalysts perhaps will be still in use for the next years [11,13].

As water vapour is an unavoidable component of diesel exhaust and its presence could also deactivate Cu-based catalysts [12], it is understood that the existence of acid sites on the catalyst surface provides points of attack and subsequent dealumination. It is of interest, therefore, to evaluate how far the catalyst could tolerate the presence of water vapour by reducing the availability of acid sites (i.e. increasing the Si/Al ratio of the parent zeolite) [14,15]. Some studies on the other hand suggested that gold on alumina catalysts are highly selective toward the formation of N₂ and have a peak of their NO_x reduction activities at 200 °C. Such materials, combined with a suitable high-temperature catalyst (i.e., CuZSM5 and/or Ag/alumina) [15], may broaden the operating window for an efficient NO_x removal under the low temperatures (below 150 °C) recorded during the driving cycle.

The CuMORD catalyst (synthetic) has been studied, though it was shown to be efficient for NO reduction using hydrocarbons as a reducing agent [16]. The natural Mordenite-based catalysts were proven to be an excellent for SCR–NO_x with ammonia or methane as reducing agent, but they may suffer deactivation by water, SO₂ or HCl [16,17].

Recent studies have reported the use of natural mordenite ion exchanged with Cu(II), Zn(II) and Ag(I). Exchanged Cuban Mordenite Natural zeolite was successfully utilized in the SCR-NO_x using ammonia as the reducing agent, demonstrating that Cu(II)-exchanged sample may yield an extremely high performance of NO conversion in the presence of 100 ppm of SO₂. It also displayed good water tolerance and was working without any diffusion problems, with very low contact times. The positive influence on the active chemical state of copper ions and improvement of microporosity for Cu-Mordenite Cuban could be the key factors explaining the better performance of the sample in the SCR of NO [15,17].

Artificial neural networks (ANNs) have been used for several system modelling. ANN has been mainly used in classification problems, in character recognition, in negotiation problems in information processing, in control and automation and in prediction problems [18]. Thus, ANN has been used to model the behaviour of one catalyst under different reaction conditions for a specific reaction. Have successfully been applied to conventional catalyst modelling and design of solid catalyst [18,19]. Those applications include: design of ammoxidation of propylene catalyst, analysis and prediction of results of the reduction of NO over zeolite, and modelation the kinetics of a chemical reaction using methods not based in kinetic model based in catalyst under different reaction conditions (partial pressure, contact time and temperature) [19]. Therefore, ANN consists of a numeral of simple interconnected processing units, called neurons, which are analogous to the biological neurons. Have been used due to its ability of supplying fast answers to a problem and generalising their answers, providing acceptable results for unknown samples [19].

Authors' research was concentrated on the analysis of the catalysts based on copper-zeolites proposed for the possible use in SCR-NO_x systems for the after-treatment of the exhaust gases from the diesel vehicles. The catalysts were prepared by ion-exchange over Natural Cuban Mordenite and ZSM-5 zeolites support. Also the catalyst stability in the presence of H₂O and SO₂ were investigated for the both prepared and commercial catalysts. Finally, a neural network-based approach to predict NO_x conversion efficiency of copper-zeolite and commercial catalyst was implemented to derive and input a mathematical function into a numerical model for diesel road vehicle simulation [20,21].

The main innovation aspect of this research consists in the use of ANN to derive experimental correlations and integrate them in a diesel engine vehicle simulator. The ANN was constructed using the experimental dataset derived under the typical exhaust of a diesel engine. The ANN was successfully trained accordingly to the experimental data in SCR-NO_x system to predict transient changes in NO_x emissions level in HDD and LDD vehicle-operating conditions according to loads/engine speeds observed in driving cycles.

This is an important methodology for predicting NO_x conversion efficiency (%), the NO_x out emissions, the NH₃ slip and N₂O emissions (in ppm, g/s, g/km or g/kWh) in a vehicle equipped with a SCR system under several traffic conditions, including those of homologation cycles.

The approach adopted used pre-euro III input conditions for diesel vehicles (HDD and LDD), equipped them with three different SCR possibilities and predicted SCR system behaviour in several roadway conditions.

The used methodology was divided in three steps/phases as follows:

Phase I: Measure experimentally huge amount of data for input gases, exhaust gases and conversion efficiency of copper based SCR systems (detailed explanation in Section 2).

Phase II: Derive mathematical correlation based on experimental data through ANN (details in Section 3).

Phase III: Integrate the derive correlations in a road vehicle simulator [20,21]: Simulate conversion efficiency, NH₃ slippage and N₂O formation throughout several driving cycles (details below). Section 4 shows these results.

2. Experimental

2.1. Catalyst preparation

Two types of zeolites were selected, a commercial ZSM-5 supplied by Zeolist International Co., with an atomic ratio Si/Al = 20, and a natural Mordenite, with an atomic ratio Si/Al = 5, from Palmarito deposit (Santiago de Cuba, Cuba). The catalysts were prepared by ion-exchange with an aqueous solution of copper(II) acetate. The copper loading was 2.0 and 4.0 wt.% for ZSM5 and MORD, respectively. The ion-exchange was carried out at room temperature using the homoionic ammonium forms NH₄⁺-ZSM5 and NH₄⁺-MORD in contact with the metal salt solution during 24 h, and pH 6. Finally, the catalysts were calcined at 550 °C for 6 h with a heating rate of 2 °C min⁻¹. The detailed preparation method is described elsewhere [12,16,22].

2.2. Catalyst characterization

The copper content was determined by atomic absorption techniques (A.A.), using a Peking-Elmer 3100 spectrometer. Powder XRD (X-ray diffraction) patterns were obtained with a Siemens D500 diffractometer, equipped with a graphite monochromator and using Cu Kα radiation. The diffractograms were recorded in the range 5° < 2θ < 50° with a scanning speed of 0.01° min⁻¹. The BET (Brunauer–Emmett–Teller) surface area of the catalysts was determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 apparatus. Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out between 50 and 800 °C using a flow of 10% H₂/Ar (48 cm³, min⁻¹) and a heating rate of 10 °C min⁻¹. Water produced in the reduction reaction was eliminated by passing the gas flow through a cold finger (80 °C). The H₂-consumption was controlled by an on-line gas chromatograph (Shimadzu GC-14A) provided with a thermal conductivity detector (TCD).

Temperature-programmed desorption of ammonia (NH₃-TPD) was carried out to evaluate the total acidity of the catalysts. The catalysts were pretreated in a flow of He at 550 °C before the adsorption of ammonia at 100 °C, the NH₃-TPD was performed between 100 and 550 °C with a heating rate of 10 °C min⁻¹ by using a helium flow. The evolved ammonia was analysed by online gas chromatography (Shimadzu GC-14A) provided with a TCD.

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300W, 15 kV, 1253.6 eV) and with a multi-channel detector. Spectra of powder samples were recorded in the constant-pass energy mode at 29.35 eV, using an analysis area of 720 μm in diameter. During processing of the XPS spectra, binding energy values were referenced to the C 1s peak (284.8 eV) from the adventitious contamination layer. Spectra of C 1s and Cu 2p regions were first recorded for 10 min. This short acquisition time was used to avoid, as much as possible, reduction of Cu²⁺ species by the action of the X-ray excitation source as previously reported [22].

2.3. Catalyst activity

The catalyst activity of the catalysts was tested in a flow micro-reactor consisting of a Pyrex glass reactor (0.30 in. o.d.) connected

on-line to a quadrupole mass spectrometer (Balzers GSB 300 02). The catalysts were pelletised with a particle size of 0.25–0.40 mm. About 150 mg of pelletised solids were set into a reactor and plugged with glass wool. The activities of the copper-catalysts were compared with a commercial $V_2O_5/WO_3/TiO_2$ catalyst (CATCO). Before the catalytic runs, the catalysts were pre-treated at 350 °C in situ for 3 h under a helium flow ($30 \text{ cm}^3 \text{ min}^{-1}$).

The reaction mixture typically consisted of 1000 ppm NO, 1000 ppm NH_3 , and 2.5 vol.% O_2 (balanced with He). Water was added to the feed, passing helium through a saturator with deionized water. Moreover, 50 ppm of the SO_2 was added to the feed to study its effect in the catalytic performance. The flows were independently controlled by channel mass flow-meters (Brooks). The system was operated at the atmospheric pressure and with a total flow of the $150 \text{ cm}^3 \text{ min}^{-1}$. The gas hourly space velocity (GHSV) was about $48,000 \text{ h}^{-1}$; under these conditions, both external and internal diffusion limitations were absent. We studied the behaviour of the catalysts for the temperatures ranged between 100 and 550 °C. The analysis of reactants and products (NO, NH_3 , O_2 , N_2 , N_2O , H_2O and SO_2) was monitored by mass spectrometer mentioned above.

To extrapolate the data measured in the reactor to a real catalyst, the space velocity parameter was used. Space velocity of a real catalyst in the diesel vehicle exhaust was referred to the wash coat volume of the SCR catalyst that is 20% of the catalyst volume [23]. The typical engine-out data was converted to typical space velocity referred to the active part of the catalyst, and these values of space velocity were the ones used in the experimental part of the research:

$$GHSV = \frac{EMF (\text{g s}^{-1})}{M_E (\text{g mol}^{-1})} \times \frac{R (\text{J mol}^{-1} \text{K}^{-1}) T (\text{K})}{P (\text{J l}^{-1})} \times \frac{1}{V (\text{l}) \times 0.2} \times 3600 (\text{s h}^{-1}) \quad (1)$$

EMF stands for exhaust mass flow, M_E stands for molar mass of exhaust flow, R is the universal constant for gases, T is the temperature of exhaust gases, and P is the exhaust gas pressure.

3. Simulation

3.1. Artificial neural network approach

Following a similar approach to engine-out emissions simulation in road vehicle simulators (steady-state fuel consumption and emissions database maps), the large amount of steady-state data obtained in the experimental part of the research was used for the neural network approach. This way mathematical correlations were obtained and directly implemented in the road vehicle simulator. This is a first approach to solve the lack of simulation models for SCR in such road vehicle simulators.

The measured results obtained from the experimental apparatus described above for copper-zeolite catalyst and commercial catalyst were used to train an ANN. The main goal is to obtain the bias and weights for each neuron and the activation functions for hidden and output layers with the lowest mean squared error (MSE). Fifteen percent of the data was not used to train the ANN, but instead to test it. The best ANN will be used to construct the correlation function between the inputs and outputs, and will be integrated in a road vehicle fuel consumption and emission model.

The relevant inputs considered for the outputs NO_x conversion efficiency, NH_3 conversion efficiency and N_2O formation were: space velocity (SV, h^{-1}), exhaust gas temperature (T , °C), oxygen concentration ($O_2\%$, v/v), water concentration ($H_2O\%$, v/v), sulphur dioxide concentration (SO_2 ppm), nitrogen oxide concentration (NO ppm), ammonia concentration (NH_3 ppm). Schematically

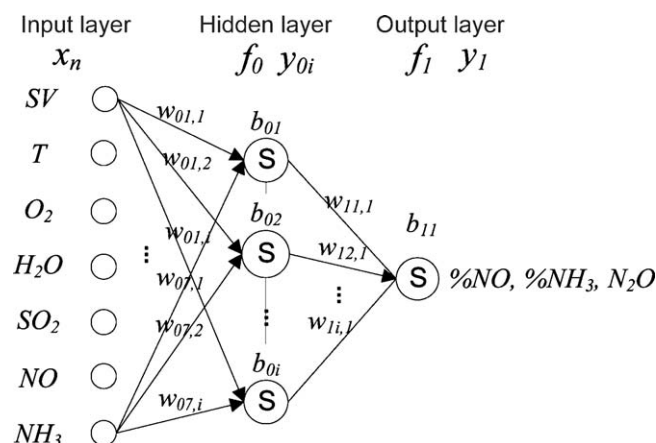


Fig. 3. ANN architecture of SCR model.

Fig. 3 shows an overview of the structural organization of the ANN used.

ANN design is constituted by an input layer with seven neurons, a single hidden layer with three neurons, and one output layer with one neuron, for each output considered. Stochastic back propagation with the Levenberg–Marquardt algorithm (MatLab®) was used to train the network. The activation functions used are

$$f_0 = \log \text{sig}(n) = \frac{1}{(1 + \exp(-n))} \quad (2)$$

For the hidden layer and for the output layer:

$$f_1 = \tan \text{sig}(n) = \frac{2}{(1 + \exp(-2n)) - 1} \quad (3)$$

The derived correlation for the ANN is

$$y_{0i} = \log \text{sig}(w_{0n,i} \times x_n + b_{0i}) \quad (4)$$

$$y_1 = \tan \text{sig}(w_{0i,1} \times y_{0i} + b_{11}) \quad (5)$$

$$\%NO, \%NH_3, N_2O$$

$$= \tan \text{sig} \left(\sum (w_{0i,1} \times \log \text{sig}(\sum (w_{0n,i} \times x_n) + b_{0i})) + b_{11} \right) \quad (6)$$

Different weights and biases are generated for each different output (y_1).

3.2. Validation

A total of more than 577 sets of measurements were performed, of which 85% were used to train and validate several networks. The networks with low sum squared error were used to obtain the correlation function between the inputs and outputs. In face of, stochastic back propagation was used to train the network, the number and size of the hidden layers being determined empirically according to error value and stability observed. A single hidden layer containing three neurons proved the best solution for the application. The 15% were used to test the SCR ANN model.

The errors when compared to the training data for the network used. The statistical analysis of the results indicates that the R^2 value for the test, training and validation data was higher, more than 0.67, and this indicates that ANN-based model developed in this work can predict the (%) NO conversion efficiency, out NH_3 (ppm) and N_2O (ppm) formation to SCR system of a diesel vehicle. Table 2 shows the obtained R^2 values for each derived correlation.

Table 2
R² value for the test, training and validation data.

Catalyst		R ² _{test}	R ² _{training}	R ² _{validation}
CATCO	NO _x	0.73	0.74	0.80
	NH ₃	0.80	0.82	0.80
	N ₂ O	0.94	0.84	0.90
CuMORD	NO _x	0.85	0.88	0.90
	NH ₃	0.84	0.90	0.85
CuZSM5	NO _x	0.85	0.93	0.90
	NH ₃	0.80	0.90	0.80
	N ₂ O	0.67	0.70	0.70

Fig. 4 shows an example of simulated and measured data for NO conversion efficiency.

4. Results and discussion

4.1. Characteristics of the prepared catalyst

Table 3 shows the BET surface areas and Cu contents (wt.%). The results show, as expected, a slight decrease in the BET surface areas as in the pore volume regarding the support, after the incorporation of Cu into the framework. In contrast, when we considered the surface area and pore volume for the CuMORD sample, they hardly change regarding the natural Mordenite zeolite, due to its unidimensional structure [16,17,22].

The X-ray diffraction patterns of the prepared catalysts and supports based ZSM-5 and natural mordenite zeolites showed any loss of crystallinity of the natural mordenite and MFI phase and the absence of the characteristic reflection lines of copper(II) oxide species [12,14,17]. The absence of metallic oxides points out the successful incorporation of metallic cations by ion-exchange on the exchange sites.

The reduction of copper species was studied by H₂-TPR. In general, the reducibility of copper(II) is function of both the nature of the support and the dispersion degree of the active phase. Fig. 5 shows the normalized H₂ consumption curves, obtained by dividing the H₂ consumption signal by the amount of copper present in the catalyst. These catalysts have different H₂ consumption peaks at different temperatures. The CuZSM5 catalyst presents a H₂ complex consumption band extending from 150 to 250 °C, and the CuMORD catalyst presents a H₂ consumption band from 120 to 250 °C. For this catalyst, different copper ions seem to be present in different environments, with broad bands of H₂ consumption appearing with various shoulders. The first species to be reduced are copper oxides in the lowest temperature peak.

As determined by NH₃-TPD, the acidity of these catalysts is depicted in Fig. 6. From this plot, the addition of Cu produces a sharp decrease in the acidity in relation to the support. The greatest desorption of ammonia occurs in the temperature range 200–300 °C for the CuMORD catalyst, while it is similar to temperature range 100–200 °C for CuZSM5 catalyst. From the results presented in Fig. 7 it can be observed that for typical space velocity values,

Table 3
Copper content and textural parameters for the supports and the catalysts.

Sample	[Cu] (wt.%)	S _{BET} (m ² g ⁻¹)	V _{micropore} ^a (cm ³ g ⁻¹)
ZSM5	–	286	0.159
MORD	–	167	0.085
CuZSM5	1.98	240	0.124
CuMORD	4.01	178	0.089

^a Determined by the Dubinin–Astakhov method, applied to microporous solids (0.01 ≤ P/P₀ ≤ 0.05).

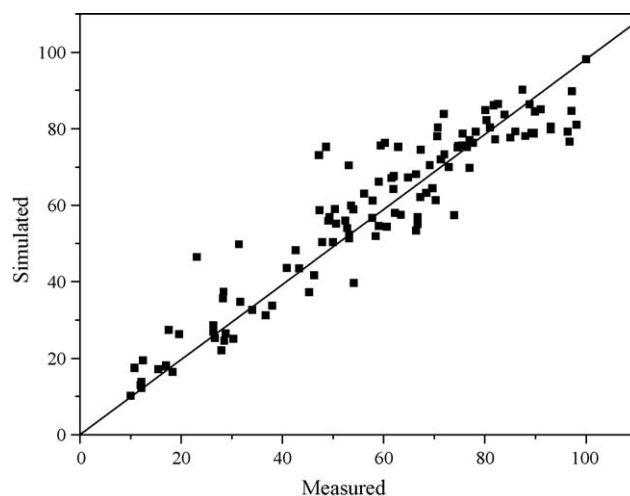


Fig. 4. Simulated and measured data for the test values of NO conversion efficiency for CuMORD.

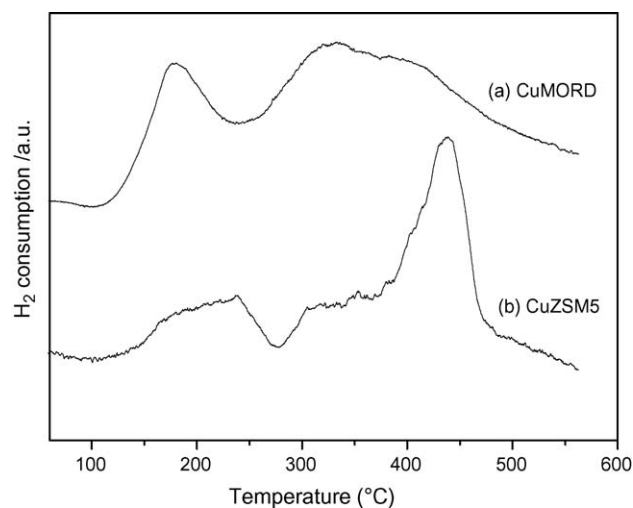


Fig. 5. TPR curves of copper-zeolite catalysts.

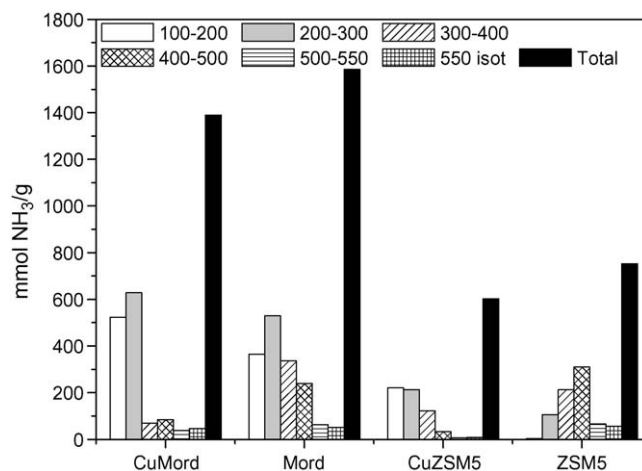


Fig. 6. NH₃ desorbed as a function of the temperature for copper-zeolite catalysts.

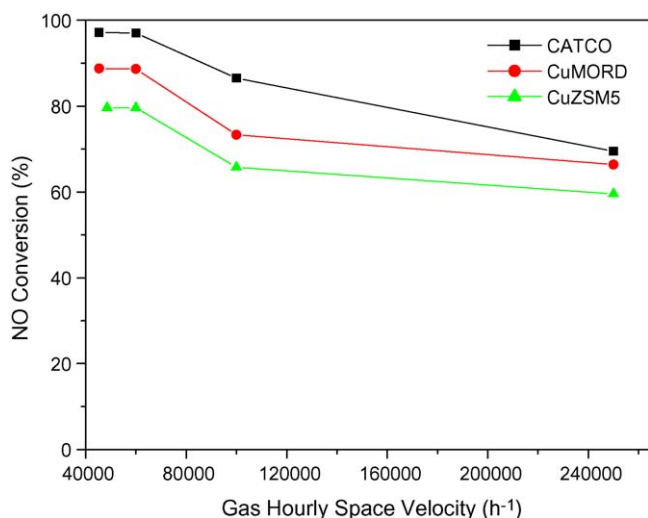


Fig. 7. NO conversion evolution with space velocity.

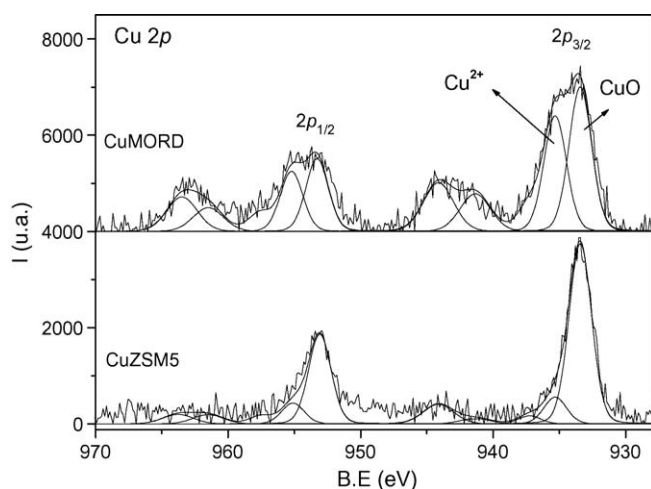


Fig. 8. Cu 2p core level spectra for CuMORD and CuZSM5 catalyst.

there was always some amount of NO conversion indicating that diffusion of NH_3 and exhaust gases occurred. The effect of space velocity was one of the main inputs of the neural network approach model.

In order to know the copper species on the surface of copper(II)-exchanged zeolites, the catalysts have been studied by XPS. The Cu $2p_{3/2}$ signal is composed of two peaks at 933.4 and 935.6 eV, where the former is assigned to the presence of CuO species, and the latter to Cu(II) ions coordinated to superficial oxygen atoms of the zeolites [15,16,22], as it is shown in Fig. 8.

4.2. Catalyst activity measurements

Fig. 9 displays the NO conversion degree as a function of reaction temperature for the catalysts tested. The high SCR activity of CATCO (commercial catalytic) is clearly discernible, especially at low temperature, up to 250 °C with 100% of NO conversion [12,22].

The results show that the CuMORD is an active catalyst at 250 °C, but at temperatures above 400 °C the catalytic oxidation of NH_3 is observed [15,22]. This reflects the non-selective reduction of NO. Similar results of NO conversion efficiency were obtained in the standard test for CuZSM5. At 350 °C, the NO conversion is about

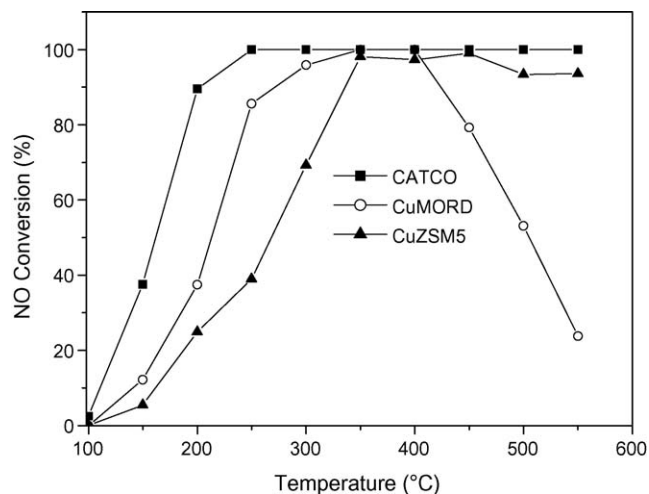


Fig. 9. NO conversion over Cu-exchanged zeolites and commercial catalyst (CATCO). Experimental conditions: 1000 ppm NO, 1000 ppm NH_3 , and 2.5 vol.% O_2 (balanced with He), flow rate $150 \text{ cm}^3 \text{ min}^{-1}$ and GHSV = $48,000 \text{ h}^{-1}$.

94%, but the catalyst CuMORD is more active at lower temperature than the catalysts CuZSM5.

The real diesel exhaust gas contains water vapour and SO_2 , so that their effects on catalyst activity must be taken into account. We performed the corresponding studies at 350 °C by adding in the feed 10% H_2O (v/v) and 50 ppm of SO_2 as shown in Figs. 10 and 11, respectively.

Figs. 10 and 11 show very high NO conversion degree at 350 °C for CuMORD (99.6% and 100%) and CATCO (91.8% and 99.8%) in the presence of H_2O vapours and SO_2 , respectively. Furthermore, no appreciable deactivation after 10 h of reaction was observed. The CuZSM5 catalyst demonstrates a slight decrease (around 20%) in its catalyst activity under the presence of SO_2 . An introduction of 10% water vapour into reaction also caused a slight deactivation of the CuZSM5 catalyst and a slight decrease in the selectivity towards nitrogen.

Table 4 summarizes the experimental results for the catalysts tested. CATCO catalyst shows a trend to form N_2O during SCR reaction. The CuZSM5 catalyst displayed high catalytic activity, with an appreciable formation of N_2O and with a significant deactivation in the presence of the water and SO_2 . Formation of N_2O may be explained by oxidation of NH_3 , as described elsewhere

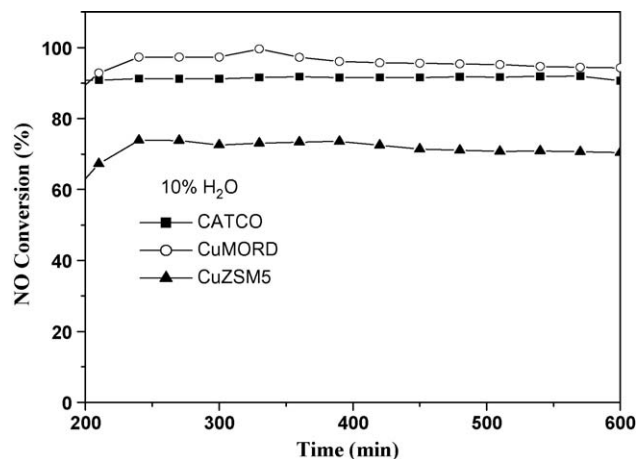


Fig. 10. Water tolerance of the Cu-exchanged zeolites and a commercial catalyst. Experimental conditions: 1000 ppm NO, 1000 ppm NH_3 , and 2.5 vol.% O_2 , 10 vol.% H_2O (balanced with He), flow rate $150 \text{ cm}^3 \text{ min}^{-1}$ and GHSV = $48,000 \text{ h}^{-1}$.

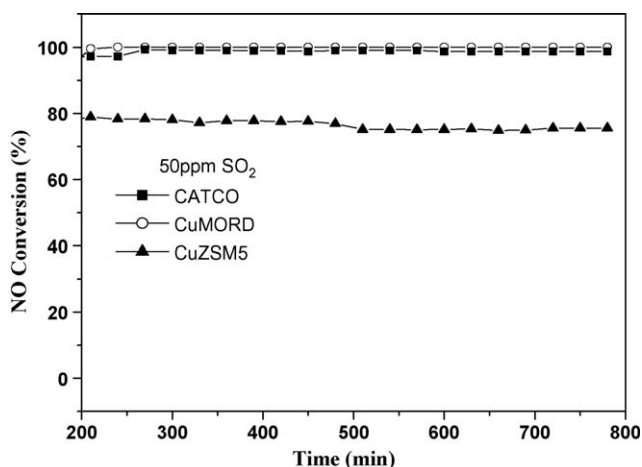


Fig. 11. The influence of SO_2 on NO conversion over Cu-exchanged zeolites and commercial catalyst. Experimental conditions: 1000 ppm NO, 1000 ppm NH_3 , 50 ppm SO_2 , and 2.5 vol.% O_2 (balanced with He), flow rate $150 \text{ cm}^3 \text{ min}^{-1}$ and GHSV = $48,000 \text{ h}^{-1}$.

[22]. CuMORD catalyst does not form N_2O in the conditions analysed, and shows the highest N_2 selectivity (100%). Some authors reported that in a copper(II)-exchanged natural Morde-nite, copper(II) ions seem to be present in a structural configuration where the formation of a Cu– H_2O complex on the catalyst surface is complicated, allowing to avoid catalyst deactivation by water [16,22].

4.3. Simulation results

Both heavy (18,000 kg, 10 l, 173 kW) and light-duty (1050 kg, 1.7 l, 60 kW) vehicles with and without a SCR– NO_x system were simulated in current European homologation cycles (for the engine and vehicle, respectively). NO_x emissions values were compared with emissions limits to analyse the corresponding emission

standard classification of the vehicles after SCR fitting. Other cycles were used such as: UDDS (Urban Dynamometer Driving Schedule), HWFET (HighWay Fuel Economy Test), a constant speed of 120 km/h HDC (Highway Driving Cycle) [5,7] and areal measured Porto city (Portugal) bus line driving cycle, were simulated and NO_x emission values again compared with Euro emission limits.

Table 5 shows some characteristics of each driving cycles, such as total duration, average speed, distance, and so forth.

Fig. 12 shows non-homologation driving cycles. As example, Fig. 12a shows the heavy-duty driving cycle of Porto city in Portugal, with simulated maximum exhaust temperatures reaching 550°C , with an average of 200°C .

Emissions simulated for light-duty vehicles are expressed in grams of pollutant per unit of travelled distance, g/km, and emissions for heavy-duty vehicle are expressed in grams per mechanical energy delivered by the engine, g/kWh.

4.4. Heavy-duty vehicle

Table 6 shows the performance of the SCR system for ESC and ETC European homologation cycles (see Fig. 2) [5]. For ESC test, an average NO_x reduction of 71, 75 and 67% were achieved for CATCO, CuMORD and CuZSM5, respectively.

These results indicate that it is possible to convert more than 60% of the engine-out emissions of NO_x and meet Euro IV emission standards in ESC cycle for a HDD equipped with SCR system using a copper–zeolite or commercial catalyst. The CATCO showed the higher conversion efficiency. The drop in average conversion efficiency under ETC transient cycle conditions for Cu-containing zeolite catalysts may be related with copper–zeolite catalyst deactivation occurring due to a change of active component, i.e., the copper ions [13,16]. Table 7 summarizes the results of NO_x emission, N_2O formation and NH_3 slippage for non-homologation driving cycles.

Some studies have shown ammonia slip together with NO_x after the catalyst measured on the FIGE cycle [6,24]. In this study, at first the ammonia slip is well below the 10 ppm goal but then it rises to

Table 4
Catalytic data at 350°C^a .

Catalyst		NO conversion (%)	NH_3 conversion (%)	N_2O formation (ppm)	N_2 selectivity (%)
CATCO	Standard	100	100	32.0	97.0
	H_2O	91.8	92.4	65.0	93.0
	SO_2	99.2	97.6	43.0	91.0
CuMORD	Standard	100	94.3	0.00	100
	H_2O	99.6	100	0.00	100
	SO_2	100	100	0.00	100
CuZSM5	Standard	98.1	94.0	47.0	95.1
	H_2O	73.8	72.6	41.0	94.6
	SO_2	78.9	77.9	0.00	100

^a Feed conditions general (standard test and stability): 1000 ppm NO, 1000 ppm NH_3 , 2.5% (v/v) O_2 , balance with helium; flow rate = 150 mL min^{-1} , 0.150 g catalyst and GHSV = $48,000 \text{ h}^{-1}$.

Table 5
Driving cycles used for vehicle (heavy and light) type approval in this work.

Drive cycle	UDDS (urban)	HWEFT (road)	NEDC	Porto bus line	HDC	ETC
Maximum speed (km/h)	91	96	120	38	120	91
Average speed (km/h)	32	78	34	11	120	60
Distance (km)	12	17	11	8	10	29
Time (s/min)	1369/23	765/13	1180/20	2466/41	300/5	1799/30
Maximum acceleration (m/s^2)	1.48	1.43	1.06	2.23	0	3.83
Max downgrade (%)	0	0	0	–15	0	0
Max upgrade (%)	0	0	0	10	0	0
Average grade (%)	0	0	0	3	0	0
Idle (s)	259	6	298	696	0	75

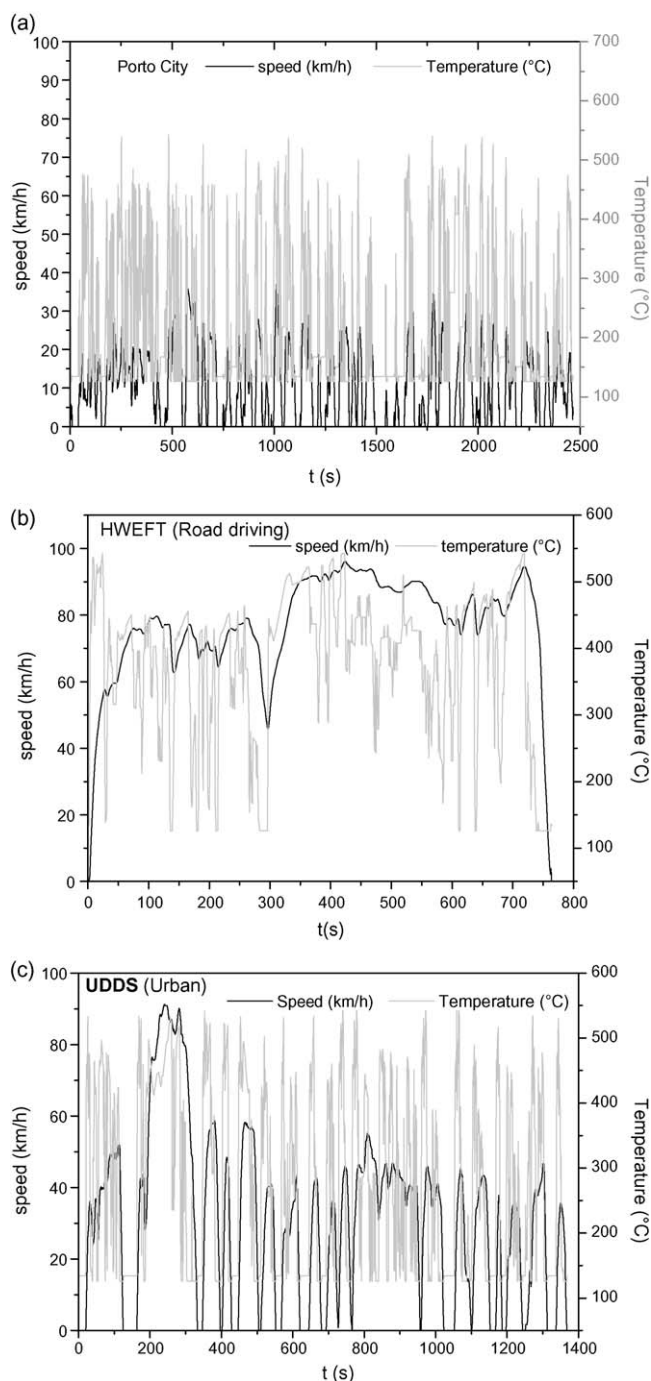


Fig. 12. Others driving cycles and temperature used in this study: (a) Porto city, (b) UDDS and (c) HWFT.

Table 6

NO_x performance of the SCR systems in ESC and ETC cycle.

Catalyst	Engine-out (g/kWh)	After SCR (g/kWh)	NO _x conversion (%)	Euro standard
ESC				
CATCO	11	3.26	71	IV
CuMORD	11	2.73	75	IV
CuZSM5	11	3.61	67	IV
ETC				
CATCO	5.43	1.36	80	V
CuMORD	5.43	3.23	40	IV
CuZSM5	5.43	3.49	31	IV

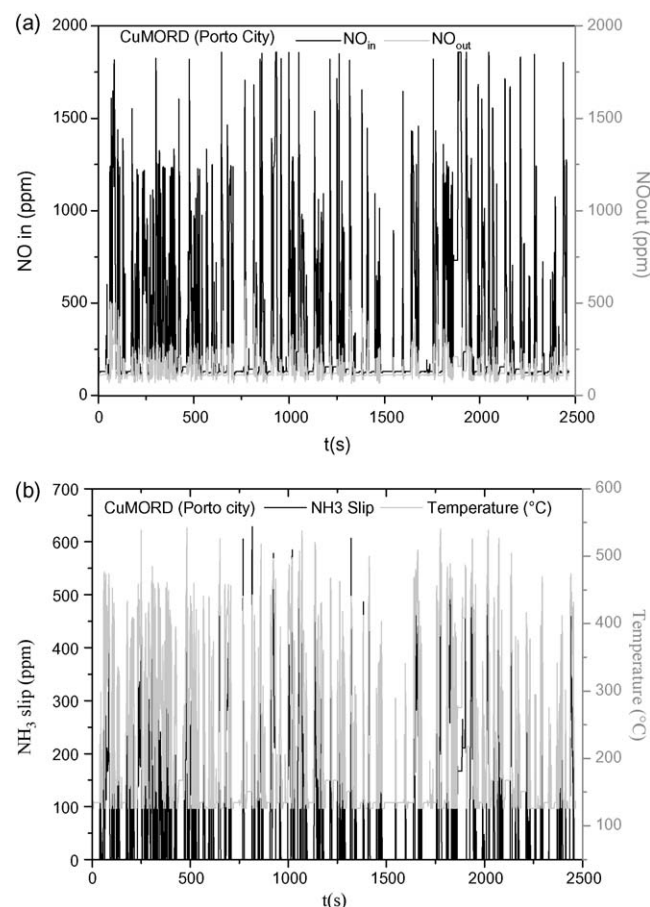


Fig. 13. Instantaneous emissions of Porto City driving cycle for CuMORD catalyst: (a) emission NO_x in g/s, (b) ammonia slip (ppm) and temperature.

a maximum of 30 ppm and on average NO_x is reduced to 85% [24]. Also in this work showed that catalyst temperature is one of the parameters affecting the conversion efficiency and the results suggest that at elevated temperatures the urea injection strategy is too aggressive in relation to the catalyst size [13,20,25].

Fig. 13 shows an example of the instantaneous emissions of NO_x before and after the SCR system for HDD vehicles equipped with CuMORD catalyst. Significant NO_x reductions were attained by using the SCR system in the driving cycle real, but as also results suggest that in one Real cycle (Porto City) at elevated temperatures the NH₃ slip can be around 600 ppm (see c). This would indicated that the ammonia introduced into the system does not match the NO_x to be converted, then there has be some ammonia slip, as desecrated in the literature [3,4,24].

4.5. Light-duty vehicle

SCR technology could be used on LDD vehicles and passenger cars without major investments in the urea distribution system. The application to LDD vehicles and passenger cars presents additional challenges. Their operational characteristics are quite different from HDD vehicles as they typically operate at high speed and low load with lower exhaust temperatures in and this can be accomplished by co-feeding NO₂, obtained from partial conversion of NO on a pre-oxidizing catalyst [4,25]. However, in this work it has been possible a preliminary study.

Table 8 shows the performance of SCR system for NEDC driving cycle is used in this study (see Fig. 1).

Table 7

Performance of the SCR system for heavy-duty vehicle.

Catalyst	Cycles driving (see Fig. 14)	NO _x in (g/kWh)	NO _x out (g/kWh)	% NO conversion Average	N ₂ O formation ($\times 10^{-4}$ g/km)	NH ₃ slip (g/km)
CATCO	UDDS	6.18	1.50	85.6	0.20	2.29
	HDC	0.14	0.06	54.0	0.02	0.07
	HWEFT	5.60	1.60	74.6	1.03	1.90
	Real Urban Circuit of Porto	6.25	1.20	90.4	0.40	3.02
CuMORD	UDDS	6.18	2.40	40.0	0.00	3.00
	HDC	0.14	0.06	53.9	0.00	0.12
	HWEFT	5.60	2.51	48.0	0.00	1.90
	Real Urban Circuit of Porto	6.25	2.15	35.0	0.00	3.51
CuZSM5	UDDS	6.18	3.80	27.0	0.13	4.10
	HDC	0.14	0.05	59.5	0.02	0.08
	HWEFT	5.60	3.32	36.2	7.04	2.84
	Real Urban Circuit of Porto	6.25	3.93	23.0	0.24	6.40

Table 8

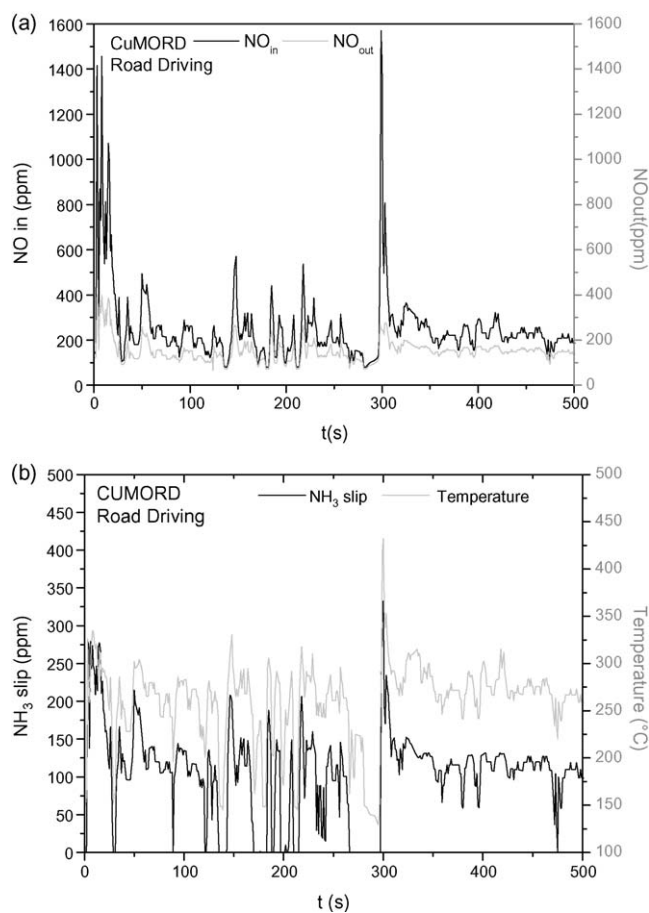
Performance of the SCR system in NEDC.

Catalyst	Engine-out (g/km)	Aftertreatment SCR-NH ₃ (g/km)	NO _x conversion (%)	Euro
CATCO	0.59	0.088	90.7	V
CuMORD	0.59	0.346	27.0	III
CuZSM5	0.59	0.413	21.0	III

Highest average conversion efficiency of NO_x emissions was 90% for CATCO catalyst. Table 9 shows exhaust NO_x emissions for all catalysts studied and simulated driving cycles. A pre-euro III LDD can comply with EuroV after fitting CATCO and to Euro III after fitting Cu-zeolite catalyst.

Fig. 14 exemplify the instantaneous NO_x emissions before and after the SCR system and ammonia slip, for LDD vehicle equipped with SCR using CuMORD. In face of Urea decomposition does not reach completion in the gas phase at temperatures that are typical for light-duty diesel exhaust (below 300 °C). In fact, only about 20% or less of the urea decomposes to HNCO and NH₃ in the gas phase at 330 °C, and only about 50% decomposes at 400 °C. HNCO has been shown to be very stable in the gas phase, requiring an oxide surface to catalyze its decomposition to NH₃ [4,24–26]. Ammonia control can be assured by an appropriated control strategy and accurate control of the dosing system or by using an oxidation catalyst downstream of the SCR catalyst to oxidise the ammonia [1]. In this case, the ammonia slip (see Fig. 14b) is less than 300 ppm which is in accordance with data found in the literature for commercial catalyst [25,26].

For LDD vehicles no experimental data in the literature was found for N₂O formation after SCR systems. Generally more N₂O is formed for over-oxidized cases when urea is injected compared with NH₃ injection [24,27]. In this work has been show N₂O formation from CATCO and CuZSM5 catalysts.

**Fig. 14.** Instantaneous emissions of road driving cycle for CuMORD catalyst: (a) NO_x emissions in ppm and (b) ammonia slip (ppm).**Table 9**

Performance of SCR system for light-duty vehicle.

Catalyst	Cycles driving	NO _x in (g/km)	NO _x out (g/km)	% NO conversion Average	N ₂ O formation (g/km) $\times 10^{-4}$	NH ₃ slip (g/km)
CATCO	UDDS	0.59	0.07	90.7	6.32	0.20
	HDC	0.74	0.27	65.0	0.41	0.29
	HWEFT	0.39	0.09	78.6	2.60	0.19
	UDDS	0.59	0.32	29.0	0.00	0.14
CuMORD	HDC	0.74	0.50	55.0	0.00	0.25
	HWEFT	0.39	0.24	32.0	0.00	0.17
	UDDS	0.59	0.34	26.0	0.21	0.36
CuZSM5	HDC	0.74	0.30	60.0	0.32	0.29
	HWEFT	0.39	0.26	28.2	2.13	0.23

5. Conclusions

Simulation results of homologation cycles show that a pre-euro HDD can comply with Euro IV after fitting the SCR system. Simulation results in real driving cycles show lower level of NO_x (up to Euro V) for HDD. Despite having toxic compounds (vanadium) and N₂O formation CATCO shows the better NO_x conversion efficiencies. CuMORD do not form N₂O and have better performance than the CuZSM5, so being a possible substitute of CATCO. LDD kept under the same regulation limits accordingly with the different catalysts (Euro III to Euro V). A pre-euro III LDD can comply with Euro V after fitting CATCO and to Euro III after fitting Cu-zeolite catalyst.

The results of the research show that the ANN integrated with a road vehicle model produce average results consistent with experimental data and can be a powerful tool for catalyst simulation of vehicle emission control technology.

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